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<b>UTILITY PATENT APPLICATION TRANSMITTAL</b> <small>(Only for new nonprovisional applications under 37 CFR 1.53(b))</small>	Attorney Docket No.	Beiersdorf 474	Total Pages	99
	First Named Inventor or Application Identifier			
	Heinrich Gers-Barlag			
	Express Mail Label No.	EI981632526-US		

<b>APPLICATION ELEMENTS</b> <small>See MPEP chapter 600 concerning utility patent application contents.</small>	<b>ADDRESS TO:</b> Assistant Commissioner for Patents Box Patent Application Washington, DC 20231
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<p>1. <input checked="" type="checkbox"/> Fee Transmittal Form <small>(Submit an original, and a duplicate for fee processing)</small></p> <p>2. <input checked="" type="checkbox"/> Specification <small>[Total Pages 43]</small> <small>(preferred arrangement set forth below)</small></p> <ul style="list-style-type: none"><li>- Descriptive title of the invention</li><li>- Cross References to Related Applications</li><li>- Statement Regarding Fed sponsored R &amp; D</li><li>- Reference to Microfiche Appendix</li><li>- Background of the invention</li><li>- Brief Summary of the invention</li><li>- Brief Description of the Drawings <small>(if filed)</small></li><li>- Detailed Description</li><li>- Claim(s)</li><li>- Abstract of the Disclosure</li></ul> <p>3. <input type="checkbox"/> Drawing(s) <small>(35 USC 113)</small> <small>[Total Sheets]</small></p> <p>4. Oath or Declaration <small>[Total Pages]</small></p> <ul style="list-style-type: none"><li>a. <input checked="" type="checkbox"/> Newly executed (original or copy)</li><li>b. <input type="checkbox"/> Copy from a prior application <small>(37 CFR 1.63(d))</small> <small>(for continuation/divisional with Box 17 completed)</small> <small>[Note Box 5 below]</small></li><li>i. <input type="checkbox"/> <b>DELETION OF INVENTOR(S)</b> <small>Signed statement attached deleting inventor(s) named in the prior application, see 37 CFR 1.63(d)(2) and 1.33(b).</small></li></ul> <p>5. <input type="checkbox"/> Incorporation By Reference <small>(useable if Box 4b is checked)</small> <small>The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4b, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein.</small></p>	<p>6. <input type="checkbox"/> Microfiche Computer Program <small>(Appendix)</small></p> <p>7. Nucleotide and/or Amino Acid Sequence Submission <small>(if applicable, all necessary)</small></p> <ul style="list-style-type: none"><li>a. <input type="checkbox"/> Computer Readable Copy</li><li>b. <input type="checkbox"/> Paper Copy <small>(identical to computer copy)</small></li><li>c. <input type="checkbox"/> Statement verifying identity of above copies</li></ul>
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<b>ACCOMPANYING APPLICATION PARTS</b>	
8. <input checked="" type="checkbox"/> Assignment Papers (cover sheet & document(s))	
9. <input type="checkbox"/> 37 CFR 3.73(b) Statement <input type="checkbox"/> Power of Attorney <small>(when there is an assignee)</small>	
10. <input type="checkbox"/> English Translation Document <small>(if applicable)</small>	
11. <input type="checkbox"/> Information Disclosure Statement (IDS)/PTO-1449 <input type="checkbox"/> Copies of IDS Citations	
12. <input checked="" type="checkbox"/> Preliminary Amendment	
13. <input checked="" type="checkbox"/> Return Receipt Postcard (MPEP 503) <small>(Should be specifically itemized)</small>	
14. <input type="checkbox"/> Small Entity <input type="checkbox"/> Statement filed in prior application, Status still proper and desired	
15. <input checked="" type="checkbox"/> Certified Copy of Priority Document(s) <small>(if foreign priority is claimed)</small>	
16. <input type="checkbox"/> Other: .....	

17. If a CONTINUING APPLICATION, check appropriate box and supply the requisite information:

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No: \_\_\_\_\_

**18. CORRESPONDENCE ADDRESS**

☐ Customer Number or Bar Code Label

☐ Correspondence address below

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**FEE TRANSMITTAL**Note: Effective October 1, 1997.  
Patent fees are subject to annual revision.**TOTAL AMOUNT OF PAYMENT (\$)** 790.00**Complete if Known**

Application Number	
Filing Date	Herewith
First Named Inventor	Heinrich Gers-Barlag
Group Art Unit	
Examiner Name	
Attorney Docket Number	Beiersdorf 474-KGB

**METHOD OF PAYMENT (check one)**

- 1.
- ☒
- The Commissioner is hereby authorized to charge indicated fees and credit any over payments to:

Deposit Account Number	19-3869
Deposit Account Name	Sprung Kramer Schaefer & Briscoe

- ☒
- Charge Any Additional Fee Required Under 37 CFR 1.16 and 1.17
- ☐
- Charge the Issue Fee Set in 37 CFR 1.18 at the Mailing of the Notice of Allowance

- 2.
- ☐
- Payment Enclosed:
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- ☐
- Check
- ☐
- Money Order
- ☐
- Other

**FEE CALCULATION****1. FILING FEE**

Large Entity		Small Entity		Fee Description	Fee Paid
Fee Code (\$)	Fee Code (\$)	Fee Code (\$)	Fee Code (\$)		
101	790	201	395	Utility filing fee	790.
106	330	206	166	Design filing fee	
107	540	207	270	Plant filing fee	
108	790	208	395	Reissue filing fee	
114	150	214	75	Provisional filing fee	
<b>SUBTOTAL (1)</b>					<b>(\$)</b> 790.

**2. CLAIMS**

Total Claims	Extra	Fes from below	Fee Paid		
11	-20 =	0	X		
Independent Claims	2	-3 =	0	X	
Multiple Dependent Claims			X		

Large Entity		Small Entity		Fee Description	Fee Paid
Fee Code (\$)	Fee Code (\$)	Fee Code (\$)	Fee Code (\$)		
103	22	203	11	Claims in excess of 20	
102	82	202	41	Independent claims in excess of 3	
104	270	204	135	Multiple dependent claim	
109	82	209	41	Reissue independent claims over original patent	
110	22	210	11	Reissue claims in excess of 20 and over original patent	
<b>SUBTOTAL (2)</b>					<b>(\$)</b>

**FEE CALCULATION (continued)****3. ADDITIONAL FEES**

Large Entity		Small Entity		Fee Description	Fee Paid
Fee Code (\$)	Fee Code (\$)	Fee Code (\$)	Fee Code (\$)		
105	130	205	65	Surcharge - late filing fee or oath	
127	50	227	25	Surcharge - late provisional filing fee or cover sheet.	
139	130	139	130	Non-English specification	
147	2,520	147	2,520	For filing a request for reexamination	
112	920*	112	920*	Requesting publication of SIR prior to Examiner action	
113	1,840*	113	1,840*	Requesting publication of SIR after Examiner action	
115	110	215	55	Extension for reply within first month	
116	400	216	200	Extension for reply within second month	
117	950	217	475	Extension for reply within third month	
118	1,510	218	755	Extension for reply within fourth month	
128	2,060	228	1,030	Extension for reply within fifth month	
119	310	219	155	Notice of Appeal	
120	310	220	155	Filing a brief in support of an appeal	
121	270	221	135	Request for oral hearing	
138	1,510	138	1,510	Petition to Institute a public use proceeding	
140	110	240	55	Petition to revive - unavoidable	
141	1,320	241	660	Petition to revive - unintentional	
142	1,320	242	660	Utility issue fee (or reissue)	
143	450	243	225	Design issue fee	
144	670	244	335	Plant issue fee	
122	130	122	130	Petitions to the Commissioner	
123	50	123	50	Petitions related to provisional applications	
126	240	126	240	Submission of Information Disclosure Stmt	
581	40	581	40	Recording each patent assignment per property (times number of properties)	
146	790	246	395	Filing a submission after final rejection (37 CFR 1.129(a))	
149	790	249	395	For each additional invention to be examined (37 CFR 1.129(b))	
Other fee (specify) _____					
Other fee (specify) _____					

\* Reduced by Basic Filing Fee Paid

**SUBTOTAL (3) (\$)****SUBMITTED BY**

Typed or Printed Name: Kurt G. Briscoe

Signature: 

Date: 12/10/97

**Complete (if applicable)**

Reg. Number: 33,141

Deposit Account User ID: 19-3869

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Beiersdorf 474-KGB:lad  
1120-Dr. Wi-ar

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants : Heinrich Gers-Barlag and Anja Müller  
Serial No. : TBA  
Filed : Herewith  
For : SUNSCREEN PREPARATIONS CONTAINING SURFACE-  
ACTIVE MONO- OR OLIGOGLYCERYL COMPOUNDS,  
WATER-SOLUBLE UV FILTER SUBSTANCES AND, IF  
DESIRED, INORGANIC MICROPIGMENTS  
Group Art Unit :  
Examiner :

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December 10, 1997

Hon. Commissioner for Patents  
Washington, D.C. 20231

**PRELIMINARY AMENDMENT**

Prior to examination, kindly amend the above-identified application as follows:

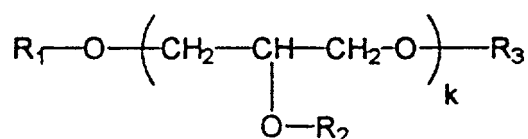
**IN THE CLAIMS**

Please cancel claim 3 and substitute.

8. A method of achieving or increasing the water resistance of

cosmetic or dermatological sunscreen preparations which are present in the form of O/W emulsions or W/O emulsions, wherein said emulsions comprise:

- (a) one or more UV filter substances which bear one or more sulphonic acid groups or sulphonate groups on their molecular backbone, and
- (b) one or more surface-active substances, selected from the group of substances of the general structural formula

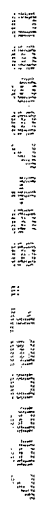


where

- k is from 1 to 8,
- $R_1$ ,  $R_2$  and  $R_3$ , independently of one another, are selected from the group consisting of:
- H, although in this case at least one of the radicals  $R_1$ ,  $R_2$  and  $R_3$  must not be H,
- branched or unbranched, saturated or unsaturated alkyl radicals,
- branched or unbranched, saturated or unsaturated acyl radicals,

[illegible]

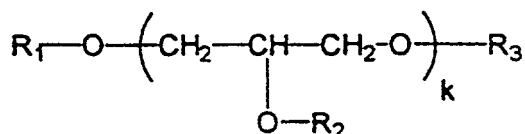
- [illegible]

[illegible][illegible]

- (c) incorporating a superficially hydrophobed inorganic pigment into the oil phase of the O/W emulsion or W/O emulsion, and
- (d) optionally, incorporating a hydrophilic inorganic pigment into the water phase of the O/W or W/O emulsion.--

Claim 4 (once amended) [Use of] The method according to Claim 8,

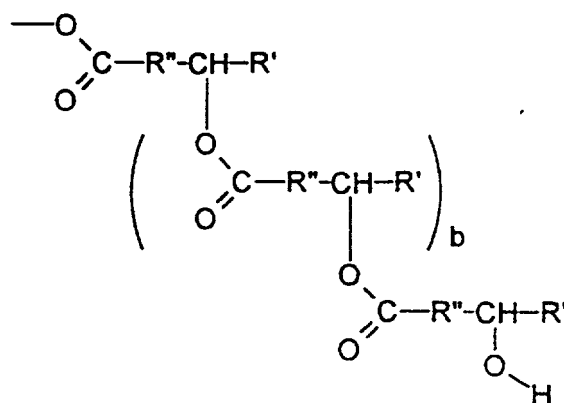
wherein the surface-active substances[,] are selected from the group of substances of the general structural formula



where

- k is from 1 to 8,
- $R_1$ ,  $R_2$  and  $R_3$ , independently of one another, are selected from the group consisting of:
- H, although in this case at least one of the radicals  $R_1$ ,  $R_2$  and  $R_3$  must not be H,
- branched or unbranched, saturated or unsaturated alkyl radicals,

- branched or unbranched, saturated or unsaturated acyl radicals, the acids of which these acyl radicals are based being selected from the group of
- branched or unbranched, saturated or unsaturated alkanecarboxylic acids having from 8 to 24 carbon atoms, in which up to 3 aliphatic hydrogen atoms can be substituted by hydroxyl groups, and/or
- polyester radicals of the general structure



where R' is selected from the group of branched and unbranched alkyl groups having from 1 to 20 carbon atoms, and R'' is selected from the group of branched and unbranched alkylene groups having from 1 to 20 carbon atoms, and b is from 0 to 200, and

[for achieving or increasing the water resistance of cosmetic or

dermatological sunscreen preparations, which are present in] the [form of]

O/W emulsions or W/O emulsions[, which] comprise

- (b) one or more UV filter substances which bear one or more sulphonic acid groups or sulphonate groups on their molecular backbone, and

[which] optionally further comprise

- (c) one or more cosmetically or pharmaceutically acceptable inorganic pigments which are superficially hydrophobed, and which are incorporated into the oil phase of the O/W emulsions or W/O emulsions, and
- (d) where any other hydrophilic inorganic pigments present are incorporated into the water phase of the O/W emulsions or W/O emulsions.

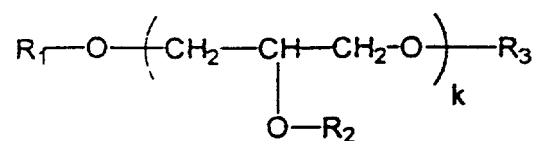
Claim 5, lines 1 and 2, after "Claim 1" delete "or 2 or uses according to Claim 3 or 4".

Claim 6, lines 1 and 2, after "Claim 1" delete "or 2 or uses according to Claim 3 or 4".

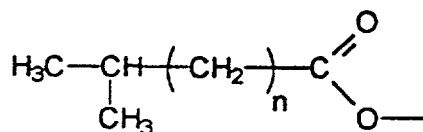
Claim 7, lines 1 and 2, after "Claim 1" delete "or 2 or uses according to Claim 3 or 4".

Add the following new claims.

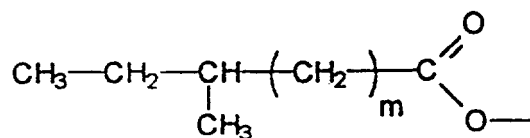
--9. The method according to Claim 8, characterized in that in the substances of the general structural formula



$R_1$ ,  $R_2$  and  $R_3$  are selected from H, methyl, ethyl, propyl, isopropyl, myristoyl, palmitoyl, stearoyl and eicosoyl groups, or from the group which is distinguished by the chemical structures

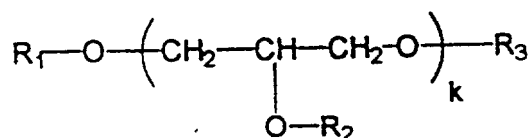


where  $n$  is from 10 to 20, the isostearyl radical being preferred, and



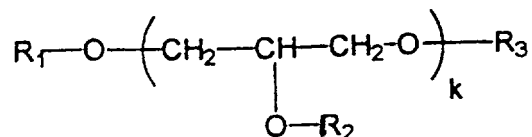
where  $m$  is from 9 to 19.--

--10. The method according to Claim 8, characterized in that the substances of the general structural formula



are selected from the group consisting of polyglyceryl-4 isostearate, polyglyceryl-3 diisostearate, polyglyceryl-2 sesquiisostearate and polyglyceryl-2 polyhydroxystearate.--

--11. The method according to Claim 8, characterized in that the substances of the general structural formula



are present in concentrations of from 0.005 to 50% by weight, preferably in concentrations of from 0.5 to 10% by weight, in particular from 1.0 to 5% by weight, based on the total weight of the preparations.--

**REMARKS**

The foregoing amendment serves to eliminate multiple dependencies.

Respectfully submitted,

SPRUNG KRAMER SCHAEFER & BRISCOE

By: \_\_\_\_\_

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Description

5     Sunscreen preparations containing surface-active  
      mono- or oligoglyceryl compounds, water-soluble UV  
      filter substances and, if desired,  
      inorganic micropigments

10     The present invention relates to cosmetic and  
      dermatological sunscreen preparations, in particular  
      cosmetic and dermatological sunscreen skincare prepara-  
      tions.

      In a particularly preferred embodiment, the  
      present invention relates to water-resistant sunscreen  
      preparations.

15     The damaging effect of the ultraviolet part of  
      solar radiation on the skin is generally known. Whereas  
      rays having a wavelength of less than 290 nm (the so-  
      called UVC region) are absorbed by the ozone layer in the  
      earth's atmosphere, rays in the region between 290 nm and  
20     320 nm, the so-called UVB region, cause erythema, simple  
      sunburn or even burns of varying severity.

      The narrower region around 308 nm is given as a  
      maximum for the erythemalous activity of sunlight.

25     Numerous compounds are known for providing  
      protection against UVB radiation, said compounds usually  
      being derivatives of 3-benzylidenecamphor, 4-aminobenzoic  
      acid, cinnamic acid, salicylic acid, benzophenone and  
      also 2-phenylbenzimidazole.

30     It is also important to have filter substances  
      for the region between about 320 nm and about 400 nm, the  
      so-called UVA region, because its rays too can cause  
      damage. For example, it has been found that UVA radiation  
      leads to damage of the elastic and collagenous fibres of  
      the connective tissue, causing premature ageing of the  
35     skin, and that it is to be regarded as a cause of nume-  
      rous phototoxic and photoallergic reactions. The damaging

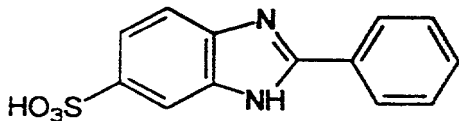
effect of UVB radiation can be reinforced by UVA radiation.

However, UV radiation can also lead to photochemical reactions, in which case the photochemical reaction products intervene in the skin's metabolism.

Such photochemical reaction products are predominantly free-radical compounds, for example hydroxyl radicals. Undefined free-radical photochemical products formed in the skin itself can also display uncontrolled subsequent reactions because of their high reactivity. However, singlet oxygen, a non-radical excited state of the oxygen molecule, can also occur under UV irradiation, as can short-lived epoxides and many other species. Singlet oxygen, for example, differs from the normal triplet oxygen (radical ground state) by its increased reactivity. However, excited, reactive (radical) triplet states of the oxygen molecule also exist.

Furthermore, UV radiation is a type of ionizing radiation. There is thus the risk that UV exposure may also create ionic species, which, in turn, are then capable of oxidative intervention in the biochemical processes.

2-Phenylbenzimidazole-5-sulphonic acid and its salts, in particular the sodium, potassium and TEA salts, obtainable for example under the name Eusolex® 232 from Merck AG, which has the following structural formula:



is a water-soluble UV filter substance which is advantageous per se.

UV absorbers or UV reflectors are mostly inorganic pigments, which are used in a known manner in cosmetics for protecting the skin from UV rays. Said inorganic pigments are oxides of titanium, zinc, iron, zirconium, silicon, manganese, aluminium and cerium and mixtures thereof, as well as modifications.

Inorganic pigments are notable per se for their

good photoprotective effect. They do however have the disadvantage that it is difficult to incorporate them satisfactorily into such formulations. Only when the particles in the final formulation are very small are they not observed to produce a disturbing "whitening" (formation of white spots on the skin) following application to the skin. The particle sizes of such pigments are usually in the range below 100 nm. In a conventional emulsion the particles tend, to a greater or lesser extent, to form agglomerates which are visible even under the light microscope. Moreover, such agglomeration does not end with the manufacturing process of a particular preparation, but continues during storage. The "whitening" can therefore increase further over a prolonged period of time. In the medium or long term, this type of agglomeration can also lead to oil loss or even emulsion breakdown.

A further disadvantage of using inorganic pigments in cosmetic formulations is that such pigments lead to severe dryness of the skin in the vast majority of cases.

Nevertheless, the disadvantage of the prior art was that normally either only comparatively low sun protection factors could be achieved, or that the sun-screen filters had an insufficient UV stability or inadequate physiological compatibility or insufficiently high solubility or dispersibility in cosmetic or dermatological preparations, or exhibited other incompatibilities with cosmetic or dermatological preparations, or had several disadvantages at the same time.

Cosmetic or dermatological preparations are frequently in the form of finely disperse multiphase systems in which one or more fatty or oily phases are present alongside one or more aqueous phases. Of these systems, the actual emulsions are, in turn, the most widespread.

In simple emulsions, one phase contains finely disperse droplets of the second phase, surrounded by an emulsifier shell (water droplets in W/O emulsions or

lipid vesicles in O/W emulsions). The droplet diameters of customary emulsions are in the range from approximately 1  $\mu\text{m}$  to approximately 50  $\mu\text{m}$ . Finer "macroemulsions", whose droplet diameters are in the range from approximately  $10^{-1}$   $\mu\text{m}$  to approximately 1  $\mu\text{m}$ , are, again without colouring additives, bluish-white in colour and opaque.

The droplet diameter of transparent or translucent microemulsions, on the other hand, is in the range from approximately  $10^{-2}$   $\mu\text{m}$  to approximately  $10^{-1}$   $\mu\text{m}$ . Such microemulsions usually have a low viscosity. The viscosity of many microemulsions of the O/W type is comparable with that of water.

A disadvantage of many O/W emulsions of the prior art is that a high content of one or more emulsifiers must always be used, since the small droplet size results in a high interface between the phases, which as a rule must be stabilized by emulsifiers.

Water-soluble UV filter substances are electrolytes which destabilize, in particular, O/W emulsions. To counteract this destabilization, polyethoxylated emulsifiers are used. However, these often have dermatological disadvantages since, although the use of customary cosmetic emulsifiers is acceptable, emulsifiers, like any chemical substance, can nevertheless cause allergic reactions or reactions based on hypersensitivity of the user in individual cases.

For example, it is known that certain photodermatoses are triggered by certain emulsifiers, but also by various fats, and simultaneous exposure to sunlight. Such photodermatoses are also called "Mallorca acne". An object of the present invention was therefore to develop sunscreen products.

Although there are completely advantageous cosmetic or dermatological preparations for protecting the skin from the harmful consequences of the effect of UV light, a disadvantage which is often observed is that the preparations are water-resistant to an inadequate extent if at all.

Sunscreen preparations are required and used particularly frequently on beaches and in open-air swimming pools. It is then desirable that the sunscreen formulation is largely water-resistant, that is to say  
5 that it is washed off from the skin only to a small extent or not at all.

Higher sun protection factors, that is to say, for example, those above SPF 15, can generally be achieved only by large amounts of UV filter substances.  
10 If a sun protection product is still to have a high sun protection factor even after bathing, the UV filter substance must, in particular, be retained on the skin.

It is already annoying if the sun protection product has to be applied again after bathing. During  
15 bathing itself, the use of a sunscreen formulation which can be washed off may even, under certain circumstances, be irresponsible and harmful to the skin, since water is a poor absorber of light in the UVA and UVB region, as a result of which it offers no notable UV protection, not  
20 even for submerged areas of skin.

For water-resistant sunscreen formulations, the prior art usually uses water-insoluble UV filter substances, water-repellent raw materials (e.g. silicone oils in high concentrations) and/or film formers, in  
25 particular high molecular weight compounds (e.g. PVP-hexadecene copolymers). Barriers are formed between the UV filter substances lying on the skin and the water.

A disadvantage here is that, although diffusion of the filter substances into the water can be delayed,  
30 it cannot be prevented completely. Such products can thus lose their protective effect considerably during prolonged bathing.

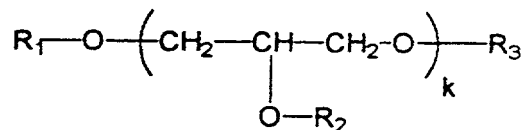
The object of the present invention was thus to overcome at least some, if not all, of these disadvantages.  
35

It was therefore surprising and unforeseeable to the expert that sun protection active ingredient combinations comprising

(a) one or more UV filter substances which bear one or

more sulphonic acid groups or sulphonate groups on their molecular backbone and

- (b) one or more surface-active substances, selected from the group of substances of the general structural formula



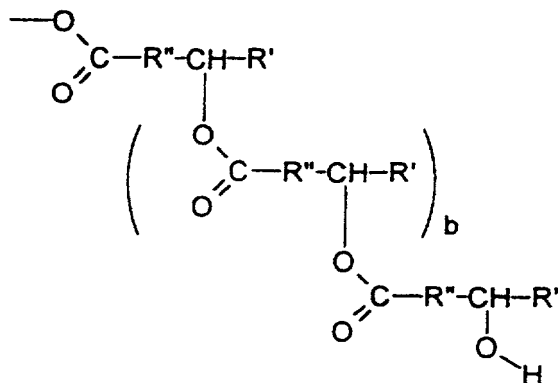
where

- k is from 1 to 8,
- $R_1$ ,  $R_2$  and  $R_3$ , independently of one another, are selected from the group consisting of:

- H, although in this case at least one of the radicals  $R_1$ ,  $R_2$  and  $R_3$  must not be H,
- branched or unbranched, saturated or unsaturated alkyl radicals,
- branched or unbranched, saturated or unsaturated acyl radicals,

the acids on which these acyl radicals are based being selected from the group of

- branched or unbranched, saturated or unsaturated alkanecarboxylic acids having from 8 to 24 carbon atoms, in which up to 3 aliphatic hydrogen atoms can be substituted by hydroxyl groups, and/or
- polyester radicals of the general structure

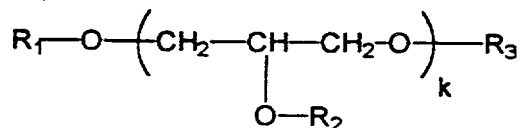


where R' is selected from the group of branched and unbranched alkyl groups having from 1 to 20 carbon atoms, and R'' is selected from the group of branched and unbranched alkylene groups having from 1 to 20 carbon atoms, and b is from 0 to 200,

overcome the disadvantages of the prior art.

According to the invention, particularly advantageous sun protection active ingredient combinations comprise

- (a) one or more UV filter substances which bear one or more sulphonic acid groups or sulphonate groups on their molecular backbone and
- (b) one or more surface-active substances, selected from the group of substances of the general structural formula

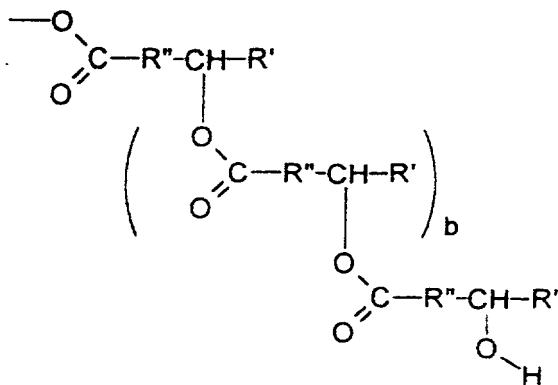


where

- k is from 1 to 8,
- R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub>, independently of one another, are selected from the group consisting of:
  - H, although in this case at least one of the radicals R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> must not be H,

- 5        the acids on which these acyl radicals are based  
being selected from the group of

- 10



15

20

- 25

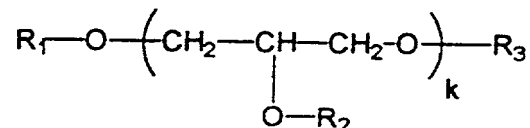
- (a) one or more cosmetically or pharmaceutically acceptable inorganic pigments which have preferably been

superficially hydrophobed  
for achieving or increasing the water resistance of  
cosmetic or dermatological sunscreen formulations which  
are present in the form of O/W emulsions or W/O emul-  
sions,

- (b) where the superficially hydrophobed inorganic pig-  
ments are incorporated into the oil phase of the O/W  
emulsions or W/O emulsions, and  
(c) where, if desired, hydrophilic inorganic pigments  
are incorporated into the water phase of the O/W  
emulsions or W/O emulsions, and

which comprise

- (d) one or more UV filter substances which bear one or  
more sulphonic acid groups or sulphonate groups on  
their molecular backbone, and  
(e) one or more surface-active substances, selected from  
the group of substances of the general structural  
formula



where

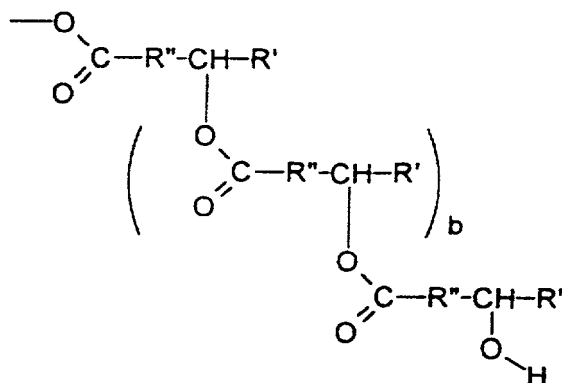
k is from 1 to 8,  
R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub>, independently of one another, are  
selected from the group consisting of:

- H, although in this case at least one of the  
radicals R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> must not be H,
- branched or unbranched, saturated or unsatu-  
rated alkyl radicals,
- branched or unbranched, saturated or unsatu-  
rated acyl radicals,

the acids on which these acyl radicals are based  
being selected from the group of

- branched or unbranched, saturated or un-  
saturated alkanecarboxylic acids having  
from 8 to 24 carbon atoms, in which up to

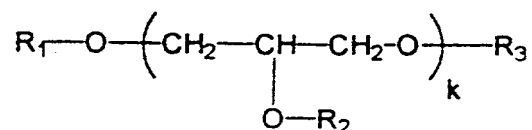
3 aliphatic hydrogen atoms can be substituted by hydroxyl groups, and/or polyester radicals of the general structure



where R' is selected from the group of branched and unbranched alkyl groups having from 1 to 20 carbon atoms, and R'' is selected from the group of branched and unbranched alkylene groups having from 1 to 20 carbon atoms, and b is from 0 to 200.

Another advantageous embodiment of the present invention is the use of

(a) one or more surface-active substances, selected from the group of substances of the general structural formula

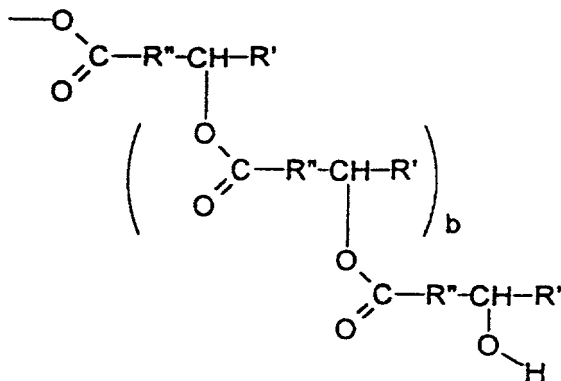


where

- k is from 1 to 8,
- R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub>, independently of one another, are selected from the group consisting of:
  - H, although in this case at least one of the radicals R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> must not be H, branched or unbranched, saturated or unsatu-

rated alkyl radicals,  
 - branched or unbranched, saturated or unsaturated acyl radicals,  
 the acids on which these acyl radicals are based  
 5 being selected from the group of

- branched or unbranched, saturated or unsaturated alkanecarboxylic acids having from 8 to 24 carbon atoms, in which up to 3 aliphatic hydrogen atoms can be substituted by hydroxyl groups, and/or
- 10 - polyester radicals of the general structure



where R' is selected from the group of  
 branched and unbranched alkyl groups having from 1 to 20 carbon atoms, and R'' is  
 15 selected from the group of branched and unbranched alkylene groups having from 1 to 20 carbon atoms, and b is from 0 to 200,

20 for achieving or increasing the water resistance of cosmetic or dermatological sunscreen formulations, which are present in the form of O/W emulsions or W/O emulsions, which comprise

(b) one or more UV filter substances which bear one or  
 25 more sulphonic acid groups or sulphonate groups on their molecular backbone, and

which optionally further comprise

(c) one or more cosmetically or pharmaceutically accept-

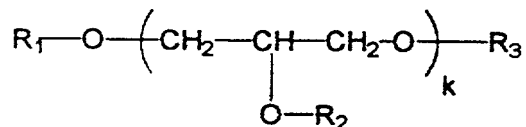
able inorganic pigments which are superficially hydrophobed, and which are incorporated into the oil phase of the O/W emulsions or W/O emulsions, and

(d) where any other hydrophilic inorganic pigments present are incorporated into the water phase of the O/W emulsions or W/O emulsions.

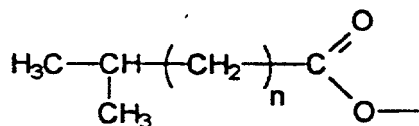
Preparations according to the invention and the described inventive uses overcome the disadvantages described for the prior art in a surprising manner. Higher sun protection factors can be achieved according to the invention than could have been assumed from the prior art.

Furthermore, it could not be foreseen from the prior art that water-resistant preparations are obtainable, according to the invention, which can achieve a considerably higher water resistance than preparations of the prior art, meaning that high sun protection factors can still be achieved even, for example, after bathing.

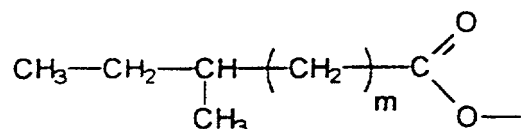
In the substances of the general structural formula



$R_1$ ,  $R_2$  and  $R_3$  can advantageously represent hydrogen atoms, but are also advantageously selected from the group consisting of methyl, ethyl, propyl and isopropyl, myristoyl, palmitoyl, stearoyl and eicosoyl, and from the group which is distinguished by the chemical structures



where  $n$  is from 10 to 20, the isostearoyl radical being preferred, and



where m is from 9 to 19.

k is preferably from 1-5, particularly preferably from 2 to 4.

Sun protection active ingredient combinations according to the invention which have proved particularly advantageous are those which are monoglyceryl esters, diglyceryl esters, triglyceryl esters and are tetraglyceryl esters and monoesters of isostearic acid, tetraglyceryl monoisostearate being particularly preferred, which in analogy to the CTFA nomenclature is also called polyglyceryl-4 isostearate.

Isostearic esters of this kind are obtainable, for example, under the product name "Isolan GI 34" from Henkel Goldschmidt Chemical Corp.

Other sun protection active ingredient combinations according to the invention which have proved particularly advantageous are those which are monoglyceryl esters, diglyceryl esters, triglyceryl esters and tetraglyceryl esters and are diesters of isostearic acid, triglyceryl diisostearate being particularly preferred, which in analogy to the CTFA nomenclature is also called polyglyceryl-3 diisostearate.

Such isostearates can, for example, be obtained under the product name "Lameform TGI" from Henkel KGaA.

Other sun protection active ingredient combinations according to the invention which have proved particularly advantageous are those which are monoglyceryl esters, diglyceryl esters, triglyceryl esters and tetraglyceryl esters and comprise mixtures of monoesters and diesters of isostearic acid, approximately equimolar mixtures being particularly preferred, such as, for example, diglyceryl sesquiisostearate, which in analogy to the CTFA nomenclature is also called polyglyceryl-2 sesquiisostearate.

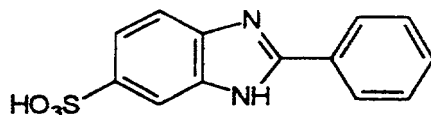
Such isostearates can, for example, be obtained under the product name "Hostacerin DGI" from Hoechst AG.

Sun protection active ingredient combinations according to the invention which have proved particularly advantageous are those whose polyester radicals are derived from hydroxystearic acid, "polyglyceryl-2 polyhydroxystearate" being particularly advantageous, which is assigned the registry numbers 156531-21-4 and 144470-58-6 in Chemical Abstracts, and which can, for example, be obtained under the trade name DEHYMULS® PGPH from Henkel KGaA.

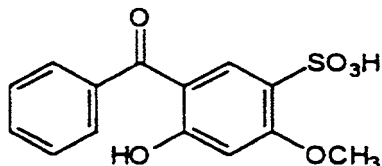
According to the invention, such surface-active substances can be present in concentrations of from 0.005 to 50% by weight, based on the total weight of the preparations. Concentrations of from 0.5 - 10% by weight, in particular from 1.0 - 5% by weight, are preferred.

Advantageous sulphonated UV filter substances in the context of the present invention are in particular:

2-phenylbenzimidazole-5-sulphonic acid and its salts, for example the sodium, potassium or its triethanolammonium salt

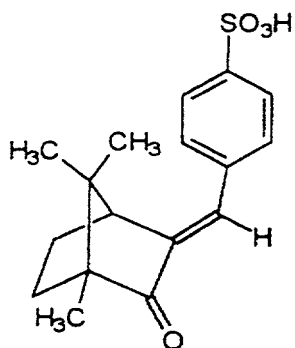


sulphonic acid derivatives of benzophenones, preferably 2-hydroxy-4-methoxybenzophenone-5-sulphonic acid and its salts, for example the corresponding sodium, potassium or triethanolammonium salt:

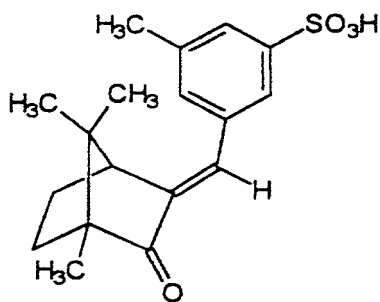


sulphonic acid derivatives of 3-benzylidenecamphor, such

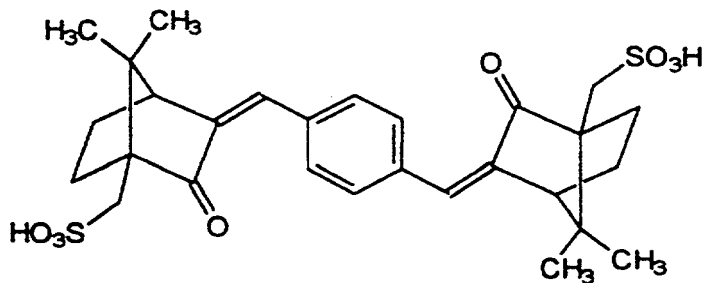
as, for example, 4-(2-oxo-3-bornylidenemethyl)benzenesulphonic acid, and its salts, for example the corresponding sodium, potassium or triethanolammonium salt:



2-methyl-5-(2-oxo-3-bornylidenemethyl)benzenesulphonic acid and its salts, for example the corresponding sodium, potassium or triethanolammonium salt:



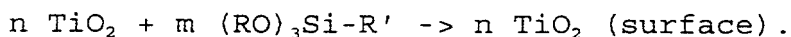
1,4-di(2-oxo-10-sulpho-3-bornylidenemethyl)benzene and its salts (the corresponding 10-sulphato compounds, for example the corresponding sodium, potassium or triethanolammonium salt), also called benzene-1,4-di(2-oxo-3-bornylidenemethyl-10-sulphonic acid):



Cosmetic and dermatological preparations according to the invention comprise inorganic pigments based on metal oxides and/or other metal compounds which are sparingly soluble or insoluble in water, in particular the oxides of titanium ( $\text{TiO}_2$ ), zinc ( $\text{ZnO}$ ), iron (e.g.  $\text{Fe}_2\text{O}_3$ ), zirconium ( $\text{ZrO}_2$ ), silicon ( $\text{SiO}_2$ ), manganese (e.g.  $\text{MnO}$ ), aluminium ( $\text{Al}_2\text{O}_3$ ), cerium (e.g.  $\text{Ce}_2\text{O}_3$ ), mixed oxides of the corresponding metals and mixtures of such oxides. Particular preference is given to pigments based on  $\text{TiO}_2$ .

According to the invention, the inorganic pigments are present in hydrophobic form, i.e. they have been rendered superficially water-repellent. This surface treatment may comprise providing the pigments with a thin hydrophobic layer by processes known per se.

Such a process comprises, for example, producing the hydrophobic surface layer by a reaction in accordance with



$n$  and  $m$  are stoichiometric parameters to be used as desired, and  $R$  and  $R'$  are the desired organic radicals. Hydrophobed pigments prepared, for example, as in DE-A 33 14 742 are preferred.

Advantageous  $\text{TiO}_2$  pigments are obtainable, for example, under the trade names T 805 from Degussa or MT 100 T from Tayca or M 160 from Kemira.

Any additional water-dispersible (i.e. hydrophilic) inorganic micropigments, if desired, may, for example, be those products which are obtainable under the trade name Tioveil® from Tioxide.

The total amount of inorganic pigments, in particular hydrophobic inorganic micropigments, in the finished cosmetic or dermatological preparations is advantageously chosen from the range of from 0.1-30% by weight, preferably from 0.1-10.0, in particular from 0.5-6.0% by weight, based on the total weight of the preparations.

In the cosmetic or dermatological preparations

according to the invention, furthermore, the more sparingly soluble components also have a better solubility than in the preparations of the prior art, even if two or more such components are present.

5           Furthermore, according to the invention, the agglomeration of inorganic pigment particles (which of course are present in dispersed and not dissolved form) with the consequences of "whitening", oil loss or emulsion breakdown, can be prevented, even if one or more  
10 components which are more sparingly soluble are also present.

Moreover, it is possible, according to the invention, to obtain sunscreen preparations which have a higher stability, in particular stability to decomposition under the influence of light, especially UV light,  
15 than could have been expected from the prior art. In particular, the stability of 4-(tert-butyl)-4'-methoxydibenzoylmethane is increased drastically.

Moreover, it is possible, according to the invention, to obtain preparations which are well tolerated by the skin, making distribution of valuable ingredients particularly easy.  
20

The total amount of water-soluble UV filter substance(s) in the finished cosmetic or dermatological preparations is advantageously chosen from the range of  
25 from 0.1-10.0% by weight, preferably from 0.5-6.0% by weight, based on the total weight of the preparations.

The total amount of 2-phenylbenzimidazole-5-sulphonic acid (if it is this substance which is to be used as sulphonated UV filter substance in the context of  
30 the present invention) or salts thereof in the finished cosmetic or dermatological preparations is advantageously chosen from the range of from 0.1-10.0% by weight, preferably from 0.5-6.0% by weight, based on the total  
35 weight of the preparations.

The total amount of 2-hydroxy-4-methoxybenzophenone-5-sulphonic acid (if it is this substance which is to be used as sulphonated UV filter substance in the context of the present invention) or salts thereof in the

finished cosmetic or dermatological preparations is advantageously chosen from the range of from 0.1-10.0% by weight, preferably from 0.5-6.0% by weight, based on the total weight of the preparations.

5           The total amount of 4-(2-oxo-3-bornylidene-methyl)benzenesulphonic acid (if it is this substance which is to be used as sulphonated UV filter substance in the context of the present invention) or salts thereof in the finished cosmetic or dermatological preparations is  
10 advantageously chosen from the range of from 0.1-10.0% by weight, preferably from 0.5-6.0% by weight, based on the total weight of the preparations.

20           The total amount of 2-methyl-5-(2-oxo-3-bornylidenemethyl)benzenesulphonic acid (if it is this substance which is to be used as sulphonated UV filter substance in the context of the present invention) or salts thereof in the finished cosmetic or dermatological preparations is advantageously chosen from the range of  
15 from 0.1-10.0% by weight, preferably from 0.5-6.0% by weight, based on the total weight of the preparations.

25           The total amount of benzene-1,4-di(2-oxo-3-bornylidenemethyl-10-sulphonic acid) (if it is this substance which is to be used as sulphonated UV filter substance in the context of the present invention) or salts thereof in the finished cosmetic or dermatological preparations is advantageously chosen from the range of  
from 0.1-10.0% by weight, preferably from 0.5-6.0% by weight, based on the total weight of the preparations.

30           The total amount of tris(2-ethylhexyl) 4,4',4"-(1,3,5-triazine-2,4,6-triyltriimino)trisbenzoate (as additional UV filter substance which is optionally to be used per se) in the finished cosmetic or dermatological preparations is advantageously chosen from the range of  
from 0.1-10.0% by weight, preferably from 0.5-6.0% by weight, based on the total weight of the preparations.  
35

          The total amount of 4-(tert-butyl)-4'-methoxydibenzoylmethane (as additional UV filter substance which is optionally to be used per se) in the finished cosmetic or dermatological preparations is advantageously chosen

from the range of from 0.1-10.0% by weight, preferably from 0.5-6.0% by weight, based on the total weight of the preparations.

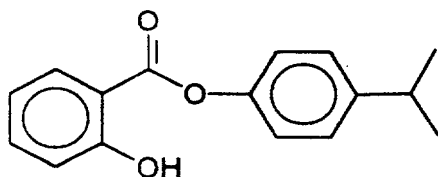
5 The total amount of 4-methylbenzylidenecamphor (as additional UV filter substance which is optionally to be used per se) in the finished cosmetic or dermatological preparations is advantageously chosen from the range of from 0.1-10.0% by weight, preferably from 0.5-6.0% by weight, based on the total weight of the preparations.  
10 tions.

The total amount of 2-ethylhexyl p-methoxycinnamate (as additional UV filter substance which is optionally to be used per se) in the finished cosmetic or dermatological preparations is advantageously chosen from  
15 the range of from 0.1-15.0% by weight, preferably from 0.5-7.5% by weight, based on the total weight of the preparations.

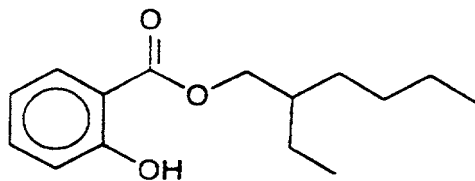
The total amount of ethylhexyl 2-cyano-3,3-diphenylacrylate (as additional UV filter substance which is optionally to be used per se) in the finished cosmetic or dermatological preparations is advantageously chosen  
20 from the range of from 0.1-15.0% by weight, preferably from 0.5-10.0% by weight, based on the total weight of the preparations.

25 Furthermore it is advantageous to combine the active ingredient combinations according to the invention with further UVA and/or UVB filters.

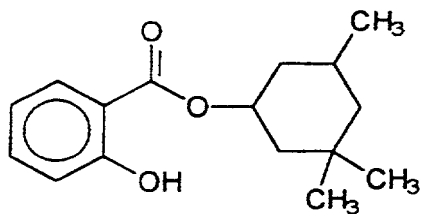
It may furthermore be advantageous, where appropriate, to combine the active ingredient combinations  
30 according to the invention with further UVA and/or UVB filters, for example certain salicylic acid derivatives, such as



(4-isopropylbenzyl salicylate),



(2-ethylhexyl salicylate, octyl salicylate),



(homomenthyl salicylate).

The total amount of one or more salicylic acid  
5 derivatives in the finished cosmetic or dermatological  
preparations is advantageously chosen from the range of  
from 0.1-15.0% by weight, preferably from 0.5-8.0% by  
weight, based on the total weight of the preparations. If  
ethylhexyl salicylate is chosen, it is advantageously to  
10 choose the total amount thereof from the range of from  
0.1-5.0% by weight, preferably from 0.5-2.5% by weight.  
If homomenthyl salicylate is chosen, it is advantageously  
to choose the total amount thereof from the range of 0.1-  
10.0% by weight, preferably 0.5-5.0% by weight.

15 It may also be advantageous to combine the  
combinations according to the invention with UVA filters  
which have usually been present in cosmetic preparations  
to date. These substances are preferably derivatives of  
dibenzoylmethane, in particular 1-(4'-tert-butylphenyl)-  
20 3-(4'-methoxyphenyl)propane-1,3-dione and 1-phenyl-3-  
(4'-isopropylphenyl)propane-1,3-dione. These combina-  
tions, and preparations which comprise these combina-  
tions, are also provided by the invention. The amounts  
used for the UVB combination can be used.

25 It is advantageous according to the invention to  
use in addition to the combinations according to the  
invention, further UVA filters and/or UVB filters, the

total amount of filter substances being, for example, from 0.1% by weight to 30% by weight, preferably from 0.5 to 10% by weight, in particular from 1 to 6% by weight, based on the total weight of the preparations, in order to provide cosmetic preparations which protect the skin from the entire range of ultraviolet radiation. They can also serve as sunscreen products.

Advantageous oil-soluble UVB filter substances are, for example:

- 10 - 3-benzylidenecamphor derivatives, preferably 3-(4-methylbenzylidene)camphor and 3-benzylidenecamphor;
- 4-aminobenzoic acid derivatives, preferably 2-ethylhexyl 4-(dimethylamino)benzoate and amyl 4-(dimethylamino)benzoate;
- 15 - esters of cinnamic acid, preferably 2-ethylhexyl 4-methoxycinnamate and isopentyl 4-methoxycinnamate;
- derivatives of benzophenone, preferably 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxy-4'-methylbenzophenone and 2,2'-dihydroxy-4-methoxybenzophenone;
- 20 - esters of benzalmalonic acid, preferably di(2-ethylhexyl) 4-methoxybenzalmalonate;
- 2,4,6-trianilino-(p-carbo-2'-ethyl-1'-hexyloxy)-1,3,5-triazine.

The list of UVB filters mentioned which can be used in combination with the active ingredient combinations according to the invention is of course not intended to be limiting.

As mentioned above, the present invention allows a comparable or even higher sunscreen filter action to be achieved than was allowed to date by the prior art, for a lower total concentration of UV filter substances. It has also proved to be particularly advantageous to introduce an additional content of cosmetically or pharmaceutically acceptable electrolytes. Over wide concentration ranges, it is possible for the concentration of the UV filter substance or substances to be reduced by the same or certainly at least a comparable amount as that with which the preparation is topped up, as it were, with one or more electrolytes. The lower

limit at which this behaviour manifests itself in a manner relevant to the consumer has as a rule proved to be a total content of about 0.5% by weight of UV filter substances.

5           The preparations according to the invention therefore advantageously comprise electrolytes, in particular one or more salts with the following anions: chlorides, and furthermore inorganic oxo element anions, and of these in particular sulphates, carbonates, phosphates, borates and aluminates. Electrolytes based on  
10       organic anions can also advantageously be used, for example lactates, acetates, benzoates, propionates, tartrates, citrates and many others. Comparable effects can also be achieved by ethylenediaminetetraacetic acid  
15       and salts thereof.

          Cations of the salts which are preferably used are ammonium, alkylammonium, alkali metal, alkaline earth metal, magnesium, iron and zinc ions. It requires no mention per se that only physiologically acceptable  
20       electrolytes should be used in cosmetics. Particular preference is given to potassium chloride, sodium chloride, magnesium sulphate, zinc sulphate and mixtures thereof. Salt mixtures such as occur in the natural salt from the Dead Sea are also advantageous.

25           The concentration of the electrolyte(s) should be from about 0.1 - 10.0% by weight, particularly advantageously from about 0.3 - 8.0% by weight, based on the total weight of the preparation.

          The cosmetic and/or dermatological sunscreen  
30       preparations according to the invention can have the customary composition and be used for cosmetic and/or dermatological sun protection, and also for treatment, care and cleansing of the skin and/or hair and as a make-up product in decorative cosmetics.

35           For use, the cosmetic and dermatological preparations according to the invention are applied to the skin and/or hair in an adequate amount in the manner customary for cosmetics.

          Those cosmetic and dermatological preparations

which are in the form of a sunscreen product are particularly preferred. These can additionally comprise at least one further UVA filter and/or at least one further UVB filter.

5           The cosmetic and dermatological preparations according to the invention can comprise cosmetic auxiliaries such as are usually used in such preparations, for example preservatives, bactericides, perfumes, dyes, pigments which have a colouring action, thickeners,  
10   humidifying and/or humectant substances, fats, oils, waxes or other customary constituents of a cosmetic or dermatological formulation, such as alcohols, polyols, polymers, foam stabilizers, electrolytes, organic solvents, further emulsifiers or silicone derivatives.

15           An additional content of antioxidants is in general preferred. Favourable antioxidants which can be used according to the invention are all the antioxidants which are suitable or customary for cosmetic and/or dermatological applications.

20           The antioxidants are advantageously chosen from the group consisting of amino acids (for example glycine, histidine, tyrosine and tryptophan) and derivatives thereof, imidazoles (for example urocanic acid) and derivatives thereof, peptides, such as D,L-carnosine,  
25   D-carnosine, L-carnosine and derivatives thereof (for example anserine); carotenoids, carotenes (for example  $\alpha$ -carotene,  $\beta$ -carotene and lycopene) and derivatives thereof, chlorogenic acid and derivatives thereof, liponic acid and derivatives thereof (for example  
30   dihydroliponic acid), aurothioglucose, propylthiouracil and other thiols (for example thioredoxin, glutathione, cysteine, cystine, cystamine and the glycosyl, N-acetyl, methyl, ethyl, propyl, amyl, butyl and lauryl, palmitoyl, oleyl,  $\gamma$ -linoleyl, cholesteryl and glyceryl esters  
35   thereof) and salts thereof, dilauryl thiodipropionate, distearyl thiodipropionate, thiodipropionic acid and derivatives thereof (esters, ethers, peptides, lipids, nucleotides, nucleosides and salts) and sulphoximine compounds (for example buthionine sulphoximines, homo-

cysteine sulfoximine, buthionine sulphones and penta-, hexa- and heptathionine sulfoximine) in very low tolerated dosages (for example pmol to  $\mu\text{mol/kg}$ ), and furthermore (metal) chelators (for example  $\alpha$ -hydroxy fatty acids, palmitic acid, phytic acid and lactoferrin),  $\alpha$ -hydroxy acids (for example citric acid, lactic acid and malic acid), humic acid, bile acid, bile extracts, bilirubin, biliverdin, EDTA, EGTA and derivatives thereof, unsaturated fatty acids and derivatives thereof (for example  $\gamma$ -linolenic acid, linoleic acid and oleic acid), folic acid and derivatives thereof, ubiquinone and ubiquinol and derivatives thereof, vitamin C and derivatives (for example ascorbyl palmitate, Mg ascorbyl phosphate and ascorbyl acetate), tocopherols and derivatives (for example vitamin E acetate), vitamin A and derivatives (vitamin A palmitate) and coniferyl benzoate of benzoin resin, rutic acid and derivatives thereof,  $\alpha$ -glycosylrutin, ferulic acid, furfurylidene-glucitol, carnosine, butylhydroxytoluene, butylhydroxyanisole, nordihydroguaiac resin acid, nordihydroguaiaretic acid, trihydroxybutyrophenone, uric acid and derivatives thereof, mannose and derivatives thereof, zinc and derivatives thereof (for example  $\text{ZnO}$  and  $\text{ZnSO}_4$ ), selenium and derivatives thereof (for example selenium-methionine), stilbene and derivatives thereof (for example stilbene oxide and trans-stilbene oxide) and the derivatives of these active ingredients mentioned which are suitable according to the invention (salts, esters, ethers, sugars, nucleotides, nucleosides, peptides and lipids).

The amount of the abovementioned antioxidants (one or more compounds) in the preparations is preferably from 0.001 to 30% by weight, particularly preferably from 0.05 - 20% by weight, in particular from 1 - 10% by weight, based on the total weight of the preparation.

If vitamin E and/or derivatives thereof are the antioxidant(s), it is advantageous to choose the particular concentrations thereof from the range of from 0.001 - 10% by weight, based on the total weight of the

preparation.

If vitamin A or vitamin A derivatives or carotenes or derivatives thereof are the antioxidant(s), it is advantageous to choose the particular concentrations thereof from the range of from 0.001 - 10% by weight, based on the total weight of the preparation.

The oil phase of the preparations according to the invention is advantageously chosen from the group consisting of esters of saturated and/or unsaturated, branched and/or unbranched alkanecarboxylic acids having a chain length of from 3 to 30 C atoms and saturated and/or unsaturated, branched and/or unbranched alcohols having a chain length of from 3 to 30 C atoms, or from the group consisting of esters of aromatic carboxylic acids and saturated and/or unsaturated branched and/or unbranched alcohols having a chain length of from 3 to 30 C atoms. Such ester oils can then advantageously be chosen from the group consisting of isopropyl myristate, isopropyl palmitate, isopropyl stearate, isopropyl oleate, n-butyl stearate, n-hexyl laurate, n-decyl oleate, isooctyl stearate, isononyl stearate, isononyl isononanoate, 2-ethylhexyl palmitate, 2-ethylhexyl laurate, 2-hexyldecyl stearate, 2-octyldodecyl palmitate, oleyl oleate, oleyl erucate, erucyl oleate, erucyl erucate and synthetic, semi-synthetic and naturally occurring mixtures of such esters, for example jojoba oil.

Furthermore, the oil phase can advantageously be chosen from the group consisting of branched and unbranched hydrocarbons and waxes, silicone oils, dialkyl ethers, from the group consisting of saturated or unsaturated, branched or unbranched alcohols, and fatty acid triglycerides, especially the triglyceryl esters of saturated and/or unsaturated, branched and/or unbranched alkanecarboxylic acids having a chain length of from 8 to 24, in particular from 12-18 C atoms. The fatty acid triglycerides can advantageously be chosen, for example, from the group consisting of synthetic, semi-synthetic and naturally occurring oils, for example olive oil,

sunflower oil, soya oil, groundnut oil, rapeseed oil, almond oil, palm oil, coconut oil, palm kernel oil and many others of this type.

5 Any desired mixtures of such oil and wax components are also advantageously to be used in the context of the present invention.

The oil phase is advantageously chosen from the group consisting of 2-ethylhexyl isostearate, octyl-  
dodecanol, isotridecyl isononanoate, isoeicosane,  
10 2-ethylhexyl cocoate, C<sub>12-15</sub>-alkyl benzoate, caprylic/capric triglyceride and dicaprylyl ether.

Mixtures of C<sub>12-15</sub>-alkyl benzoate and 2-ethylhexyl isostearate, mixtures of C<sub>12-15</sub>-alkyl benzoate and isotridecyl isononanoate and mixtures of C<sub>12-15</sub>-alkyl benzoate,  
15 2-ethylhexyl isostearate and isotridecyl isononanoate are particularly advantageous.

Of the hydrocarbons, paraffin oil, squalane and squalene are advantageously to be used in the context of the present invention.

20 Furthermore, the oil phase can advantageously contain cyclic or linear silicone oils or consist entirely of such oils, although it is preferable to use an additional content of other oil phase components in addition to the silicone oil or silicone oils.

25 Cyclomethicone (octamethylcyclotetrasiloxane) is advantageously used as a silicone oil to be used according to the invention. However, other silicone oils are also advantageously to be used in the context of the present invention, for example hexamethylcyclotri-  
30 siloxane, polydimethylsiloxane and poly(methylphenylsiloxane).

Mixtures of cyclomethicone and isotridecyl isononanoate and of cyclomethicone and 2-ethylhexyl isostearate are furthermore particularly advantageous.

35 The content of the oil phase is advantageously between 1 and 50% by weight, based on the total weight of the preparations, preferably 2.5-30% by weight, particularly preferably 5-15% by weight.

The aqueous phase of the preparations according

to the invention optionally advantageously comprises alcohols, diols or polyols of low C number, as well as ethers thereof, preferably ethanol, isopropanol, propylene glycol, glycerol, ethylene glycol, ethylene glycol monoethyl or monobutyl ether, propylene glycol monomethyl, monoethyl or monobutyl ether, diethylene glycol monomethyl or monoethyl ether and analogous products, and also alcohols of low C number, for example ethanol, isopropanol, 1,2-propanediol and glycerol, and, in particular, one or more thickeners, which can advantageously be chosen from the group consisting of silicon dioxide, aluminium silicates, polysaccharides and derivatives thereof, for example hyaluronic acid, xanthan gum and hydroxypropylmethylcellulose, particularly advantageously from the group consisting of polyacrylates, preferably a polyacrylate from the group consisting of the so-called Carbopols, for example Carbopols of types 980, 981, 1382, 2984 and 5984, in each case individually or in combination.

The following examples are intended to illustrate the present invention without limiting it. Unless stated otherwise, all the amounts, contents and percentage contents are based on the weight and the total amount or on the total weight of the preparations.

Example 1

	% by weight
Polyglyceryl-4 isostearate	5.00
Caprylic/capric triglycerides	5.00
Octyldodecanol	5.00
Dicaprylyl ether	2.00
30 Phenylbenzimidazolesulphonic acid	4.00
TiO <sub>2</sub> (hydrophobic)	3.00
Glycerin	3.00
Tocopheryl acetate	1.00
NaOH	q.s.
35 Perfume, preservative	q.s.
Water	to 100.00

Example 2

	% by weight
Polyglyceryl-4 isostearate	5.00
Caprylic/capric triglycerides	1.67
Octyldodecanol	1.67
5 Dicaprylyl ether	1.67
Phenylbenzimidazolesulphonic acid	4.00
TiO <sub>2</sub> (hydrophobic)	5.00
TiO <sub>2</sub> (hydrophilic)	5.00
Butylene glycol	3.00
10 Tocopheryl acetate	1.00
NaOH	q.s.
Perfume, preservative	q.s.
Water	to 100.00

Example 3

	% by weight
15 Polyglyceryl-4 isostearate	3.00
Caprylic/capric triglycerides	5.00
Octyldodecanol	5.00
Dicaprylyl ether	1.67
Benzene-1,4-di(2-oxo-3-bornylidene-	4.00
20 methyl-10-sulphonic acid)	
TiO <sub>2</sub> (hydrophobic)	5.00
Glyceryl monostearate	2.00
Glycerin	3.00
Tocopheryl acetate	1.00
25 NaOH	q.s.
Perfume, preservative	q.s.
Water	to 100.00

Example 4

		% by weight
	Polyglyceryl-4 isostearate	5.00
	Caprylic/capric triglycerides	1.67
	Octyldodecanol	1.67
5	C <sub>12-15</sub> -Alkyl benzoates	5.00
	Phenylbenzimidazolesulphonic acid	2.00
	TiO <sub>2</sub> (hydrophobic)	2.50
	Tris[anilino(p-carbo-2'-ethyl- 1'-hexyloxy)]triazine	3.00
10	4-(tert-Butyl)-4'-methoxydibenzoyl- methane	2.00
	Butylene glycol	3.00
	4-Methylbenzylidenecamphor	2.00
	Tocopheryl acetate	1.00
15	Sorbitan monostearate	2.00
	NaOH	q.s.
	Perfume, preservative	q.s.
	Water	to 100.00

Example 5

		% by weight
20	Polyglyceryl-3 diisostearate	5.00
	Caprylic/capric triglycerides	5.00
	Octyldodecanol	5.00
	Dicaprylyl ether	2.00
	Phenylbenzimidazolesulphonic acid	4.00
25	TiO <sub>2</sub> (hydrophobic)	3.00
	Glycerin	3.00
	Tocopheryl acetate	1.00
	NaOH	q.s.
	Perfume, preservative	q.s.
30	Water	to 100.00

Example 6

	% by weight
Polyglyceryl-3 diisostearate	5.00
Caprylic/capric triglycerides	1.67
Octyldodecanol	1.67
5 Dicaprylyl ether	1.67
Phenylbenzimidazolesulphonic acid	4.00
TiO <sub>2</sub> (hydrophobic)	5.00
TiO <sub>2</sub> (hydrophilic)	5.00
Butylene glycol	3.00
10 Tocopheryl acetate	1.00
NaOH	q.s.
Perfume, preservative	q.s.
Water	to 100.00

Example 7

	% by weight
15 Polyglyceryl-3 diisostearate	3.00
Caprylic/capric triglycerides	5.00
Octyldodecanol	5.00
Dicaprylyl ether	1.67
Benzene-1,4-di(2-oxo-3-bornylidene-	4.00
20 methyl-10-sulphonic acid)	
TiO <sub>2</sub> (hydrophobic)	5.00
Glycerin monostearate	2.00
Glycerin	3.00
Tocopheryl acetate	1.00
25 NaOH	q.s.
Perfume, preservative	q.s.
Water	to 100.00

Example 8

		% by weight
	Polyglyceryl-3 diisostearate	5.00
	Caprylic/capric triglycerides	1.67
	Octyldodecanol	1.67
5	C <sub>12-15</sub> -Alkyl benzoates	5.00
	Phenylbenzimidazolesulphonic acid	2.00
	TiO <sub>2</sub> (hydrophobic)	2.50
	Tris[anilino(p-carbo-2'-ethyl- 1'-hexyloxy)]triazine	3.00
10	4-(tert-Butyl)-4'-methoxydibenzoyl- methane	2.00
	Butylene glycol	3.00
	4-Methylbenzylidenecamphor	2.00
	Tocopheryl acetate	1.00
15	Sorbitan monostearate	2.00
	NaOH	q.s.
	Perfume, preservative	q.s.
	Water	to 100.00

Example 9

		% by weight
20	Polyglyceryl-2 sesquiisostearate	5.00
	Caprylic/capric triglycerides	5.00
	Octyldodecanol	5.00
	Dicaprylyl ether	2.00
	Phenylbenzimidazolesulphonic acid	4.00
25	TiO <sub>2</sub> (hydrophobic)	3.00
	Glycerin	3.00
	Tocopheryl acetate	1.00
	NaOH	q.s.
	Perfume, preservative	q.s.
30	Water	to 100.00

Example 10

	% by weight
Polyglyceryl-2 sesquiosostearate	5.00
Caprylic/capric triglycerides	1.67
Octyldodecanol	1.67
5 Dicaprylyl ether	1.67
Phenylbenzimidazolesulphonic acid	4.00
TiO <sub>2</sub> (hydrophobic)	5.00
TiO <sub>2</sub> (hydrophilic)	5.00
Butylene glycol	3.00
10 Tocopheryl acetate	1.00
NaOH	q.s.
Perfume, preservative	q.s.
Water	to 100.00

Example 11

	% by weight
15 Polyglyceryl-2 sesquiosostearate	3.00
Caprylic/capric triglycerides	5.00
Octyldodecanol	5.00
Dicaprylyl ether	1.67
Benzene-1,4-di(2-oxo-3-bornylidene-	4.00
20 methyl-10-sulphonic acid)	
TiO <sub>2</sub> (hydrophobic)	5.00
Glyceryl monostearate	2.00
Glycerin	3.00
Tocopheryl acetate	1.00
25 NaOH	q.s.
Perfume, preservative	q.s.
Water	to 100.00

Example 12

		% by weight
	Polyglyceryl-2 sesquiisostearate	5.00
	Caprylic/capric triglycerides	1.67
	Octyldodecanol	1.67
5	C <sub>12-15</sub> -Alkyl benzoates	5.00
	Phenylbenzimidazolesulphonic acid	2.00
	TiO <sub>2</sub> (hydrophobic)	2.50
	Tris[anilino(p-carbo-2'-ethyl- 1'-hexyloxy)]triazine	3.00
10	4-(tert-Butyl)-4'-methoxydibenzoyl- methane	2.00
	Butylene glycol	3.00
	4-Methylbenzylidenecamphor	2.00
	Tocopheryl acetate	1.00
15	Sorbitan monostearate	2.00
	NaOH	q.s.
	Perfume, preservative	q.s.
	Water	to 100.00

Example 13

		% by weight
20	Polyglyceryl-2 polyhydroxystearate	5.00
	Caprylic/capric triglycerides	5.00
	Octyldodecanol	5.00
	Dicaprylyl ether	2.00
	Phenylbenzimidazolesulphonic acid	4.00
25	TiO <sub>2</sub> (hydrophobic)	3.00
	Glycerin	3.00
	Tocopheryl acetate	1.00
	NaOH	q.s.
	Perfume, preservative	q.s.
30	Water	to 100.00

Example 14

		% by weight
	Polyglyceryl-2 polyhydroxystearate	5.00
	Caprylic/capric triglycerides	1.67
	Octyldodecanol	1.67
5	Dicaprylyl ether	1.67
	Phenylbenzimidazolesulphonic acid	4.00
	TiO <sub>2</sub> (hydrophobic)	5.00
	TiO <sub>2</sub> (hydrophilic)	5.00
	Butylene glycol	3.00
10	Tocopheryl acetate	1.00
	NaOH	q.s.
	Perfume, preservative	q.s.
	Water	to 100.00

Example 15

		% by weight
15	Polyglyceryl-2 polyhydroxystearate	3.00
	Caprylic/capric triglycerides	5.00
	Octyldodecanol	5.00
	Dicaprylyl ether	1.67
	Benzene-1,4-di(2-oxo-3-bornylidene-	4.00
20	methyl-10-sulphonic acid	
	TiO <sub>2</sub> (hydrophobic)	5.00
	Glyceryl monostearate	2.00
	Glycerin	3.00
	Tocopheryl acetate	1.00
25	NaOH	q.s.
	Perfume, preservative	q.s.
	Water	to 100.00

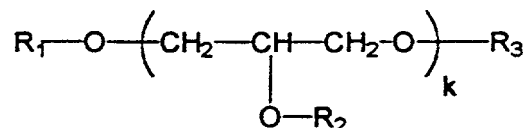
Example 16

		% by weight
	Polyglyceryl-2 polyhydroxystearate	5.00
	Caprylic/capric triglycerides	1.67
	Octyldodecanol	1.67
5	C <sub>12-15</sub> -Alkyl benzoates	5.00
	Phenylbenzimidazolesulphonic acid	2.00
	TiO <sub>2</sub> (hydrophobic)	2.50
	Tris[anilino(p-carbo-2'-ethyl- 1'-hexyloxy)]triazine	3.00
10	4-(tert-Butyl)-4'-methoxydibenzoyl- methane	2.00
	Butylene glycol	3.00
	4-Methylbenzylidenecamphor	2.00
	Tocopheryl acetate	1.00
15	Sorbitan monostearate	2.00
	NaOH	q.s.
	Perfume, preservative	q.s.
	Water	to 100.00

Patent Claims:

1. Sun protection active ingredient combinations comprising

- 5 (a) one or more UV filter substances which bear one or more sulphonic acid groups or sulphonate groups on their molecular backbone and
- (b) one or more surface-active substances, selected from the group of substances of the general structural formula

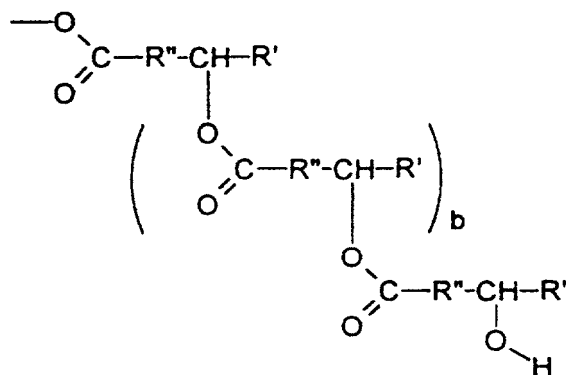


10 where

- k is from 1 to 8,
- $R_1$ ,  $R_2$  and  $R_3$ , independently of one another, are selected from the group consisting of:
  - H, although in this case at least one of the radicals  $R_1$ ,  $R_2$  and  $R_3$  must not be H,
  - branched or unbranched, saturated or unsaturated alkyl radicals,
  - branched or unbranched, saturated or unsaturated acyl radicals,

15 20 the acids on which these acyl radicals are based being selected from the group of

- branched or unbranched, saturated or unsaturated alkanecarboxylic acids having from 8 to 24 carbon atoms, in which up to 3 aliphatic hydrogen atoms can be substituted by hydroxyl groups, and/or
  - polyester radicals of the general structure
- 25



where R' is selected from the group of branched and unbranched alkyl groups having from 1 to 20 carbon atoms, and R'' is selected from the group of branched and unbranched alkylene groups having from 1 to 20 carbon atoms, and b is from 0 to 200.

2. Sun protection active ingredient combinations according to Claim 1 which also comprise one or more cosmetically or pharmaceutically acceptable inorganic pigments, which have preferably been superficially hydrophobed.

3. Use of

(a) one or more cosmetically or pharmaceutically acceptable inorganic pigments which have preferably been superficially hydrophobed

for achieving or increasing the water resistance of cosmetic or dermatological sunscreen preparations which are present in the form of O/W emulsions or W/O emulsions,

(b) where the superficially hydrophobed inorganic pigments are incorporated into the oil phase of the O/W emulsions or W/O emulsions, and

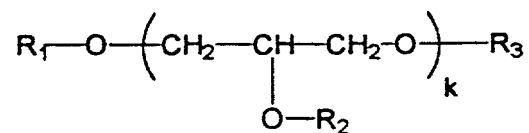
(c) where, if desired, hydrophilic inorganic pigments are incorporated into the water phase of the O/W emulsions or W/O emulsions, and

which comprise

(d) one or more UV filter substances which bear one or

more sulphonic acid groups or sulphonate groups on their molecular backbone, and

- (e) one or more surface-active substances, selected from the group of substances of the general structural formula

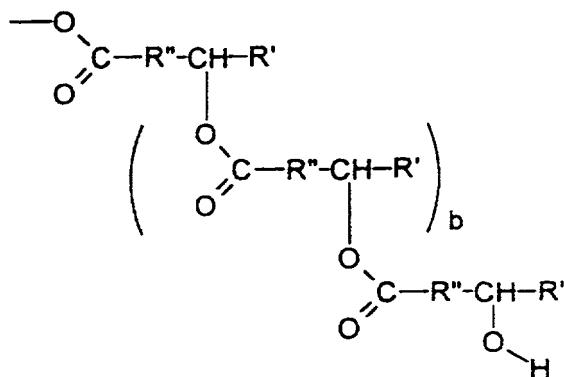


where

- k is from 1 to 8,
- $R_1$ ,  $R_2$  and  $R_3$ , independently of one another, are selected from the group consisting of:
  - H, although in this case at least one of the radicals  $R_1$ ,  $R_2$  and  $R_3$  must not be H,
  - branched or unbranched, saturated or unsaturated alkyl radicals,
  - branched or unbranched, saturated or unsaturated acyl radicals,

the acids on which these acyl radicals are based being selected from the group of

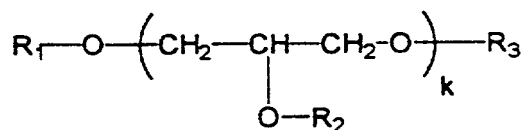
- branched or unbranched, saturated or unsaturated alkanecarboxylic acids having from 8 to 24 carbon atoms, in which up to 3 aliphatic hydrogen atoms can be substituted by hydroxyl groups, and/or
- polyester radicals of the general structure



where R' is selected from the group of branched and unbranched alkyl groups having from 1 to 20 carbon atoms, and R" is selected from the group of branched and unbranched alkylene groups having from 1 to 20 carbon atoms, and b is from 0 to 200.

4. Use of

- (a) one or more surface-active substances, selected from the group of substances of the general structural formula

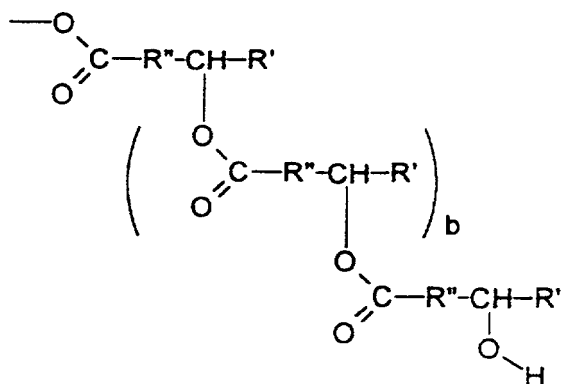


where

- k is from 1 to 8,
- R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub>, independently of one another, are selected from the group consisting of:
  - H, although in this case at least one of the radicals R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> must not be H,
  - branched or unbranched, saturated or unsaturated alkyl radicals,
  - branched or unbranched, saturated or unsaturated acyl radicals,

the acids on which these acyl radicals are based being selected from the group of

- branched or unbranched, saturated or unsaturated alkanecarboxylic acids having from 8 to 24 carbon atoms, in which up to 3 aliphatic hydrogen atoms can be substituted by hydroxyl groups, and/or
- polyester radicals of the general structure



where R' is selected from the group of branched and unbranched alkyl groups having from 1 to 20 carbon atoms, and R'' is selected from the group of branched and unbranched alkylene groups having from 1 to 20 carbon atoms, and b is from 0 to 200,

for achieving or increasing the water resistance of cosmetic or dermatological sunscreen preparations, which are present in the form of O/W emulsions or W/O emulsions, which comprise

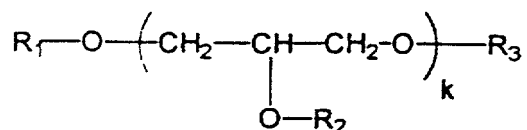
(b) one or more UV filter substances which bear one or more sulphonic acid groups or sulphonate groups on their molecular backbone, and

which optionally further comprise

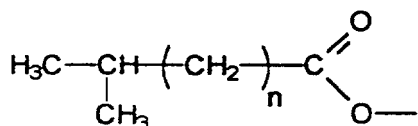
(c) one or more cosmetically or pharmaceutically acceptable inorganic pigments which are superficially hydrophobed, and which are incorporated into the oil phase of the O/W emulsions or W/O emulsions, and

(d) where any other hydrophilic inorganic pigments present are incorporated into the water phase of the O/W emulsions or W/O emulsions.

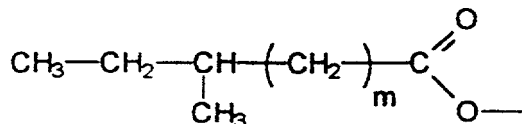
5. Preparations according to Claim 1 or 2 or uses according to Claim 3 or 4, characterized in that in the substances of the general structural formula



5  $R_1$ ,  $R_2$  and  $R_3$  are selected from H, methyl, ethyl, propyl, isopropyl, myristoyl, palmitoyl, stearoyl and eicosoyl groups, or from the group which is distinguished by the chemical structures

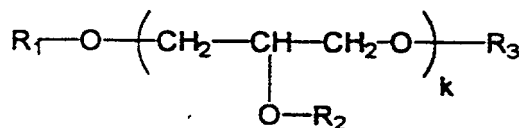


where  $n$  is from 10 to 20, the isostearyl radical being preferred, and



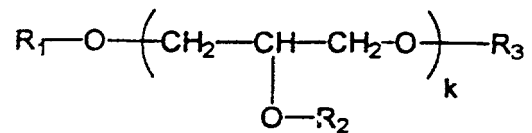
10 where  $m$  is from 9 to 19.

6. Preparations according to Claim 1 or 2 or uses according to Claim 3 or 4, characterized in that the substances of the general structural formula



15 are selected from the group consisting of polyglyceryl-4 isostearate, polyglyceryl-3 diisostearate, polyglyceryl-2 sesquiisostearate and polyglyceryl-2 polyhydroxystearate.

7. Preparations according to Claim 1 or 2 or uses according to Claim 3 or 4, characterized in that the substances of the general structural formula



are present in concentrations of from 0.005 to 50% by weight, preferably in concentrations of from 0.5 to 10% by weight, in particular from 1.0 to 5% by weight, based on the total weight of the preparations.

**Abstract:**

Sun protection active ingredient combinations comprising

- (a) one or more UV filter substances which bear one or more sulphonic acid groups or sulphonate groups on their molecular backbone and
- (b) one or more surface-active substances selected from the group of mono- or oligoglyceryl esters.

## COMBINATION DECLARATION & POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled „**Sunscreen preparations containing surface-active mono- or oligo-glyceryl compounds, water-soluble UV filter substances and, if desired, inorganic micropigments**“ the specification of which is attached hereto.

-OR-

was filed on \_\_\_\_\_ as

Application Serial No. \_\_\_\_\_ and was amended \_\_\_\_\_

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)			Priority Claimed
<u>196 51 478.9</u> (Number)	<u>Germany</u> (Country)	<u>11/12/1996</u> (Day/Month/Yr. Filed)	[X] yes [ ] no
_____ (Number)	_____ (Country)	_____ (Day/Month/Yr. Filed)	[X] yes [ ] no

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

_____ (Application Serial No.)	_____ (Filing Date)	_____ (Status) (patented, pending, abandoned)
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punished by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

**POWER OF ATTORNEY:** As a named Inventor, I hereby appoint the following attorneys and/or agents to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

Arnold Sprung, Reg. No. 17,232; Nathaniel D. Kramer, Reg. No. 25,350; Ira J. Schaefer, Reg. No. 26,802, and Esther Steinhauer, Reg. No. 40,255 all of 120 White Plains Road, Tarrytown, New York 10591; Kurt G. Briscoe, Reg. No. 33,141; William C. Gerstenzang, Reg. No. 27,552; Mark W. Russell, Reg. No. 37,514; Paul J. Juettner, Reg. No. 20,974 of 660 White Plains Road, New York 10591, my attorneys with full power of substitution and revocation

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